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Analysis and Performance Evaluations of Chemical Agent Resistant Coating Systems

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Analysis and Performance Evaluations of Chemical Agent Resistant Coating Systems

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Abstract

Polyurethane coatings used as camouflage and protective "top coats" for Army tactical vehicles and aircraft have been characterized and evaluated for performance criteria. A two-component water-reducible and a one-component solvent-based polyurethane coating have been investigated. The water-reducible (WR) coating was developed and patented by the U.S. Army Research Laboratory, Weapons and Materials Research Directorate at Aberdeen Proving Ground, MD; it exhibits a 50% reduction in volatile organic compounds (VOCs) compared to the solvent-based (SOL) system. Compared to the solvent-based formulation, the WR polyurethane maintains required chemical agent resistance and exhibits superior properties. The coating performance properties investigated include flexibility, weather durability, hardness, impact, and mar resistance. The coatings were characterized using dynamic mechanical analysis (DMA), Fourier-transform infrared spectroscopy (FTIR), and desorption-gas chromatography-mass spectroscopy (D-GC-MS). Chemical characterization and mechanical evaluation lend insight into the relationship between molecular interaction during film formation and the resulting coating properties. The effect of coating dry time was investigated using DMA. FTIR was utilized to characterize "unaged" coatings and to better understand the effect of accelerated weathering on the chemistry of the WR and SOL coatings.

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1. Introduction

The U.S. Army utilizes polyurethane coatings as camouflage "top coats" on all U.S. Army tactical vehicles and aircraft. These coatings not only serve to camouflage vehicles, but also provide protection against chemical warfare agents. The coatings must retain their physical properties over a broad temperature range in widely varying climatic environments. Currently, camouflage topcoats used on U.S. Army vehicles are comprised of a two-component or one-component solvent-based (SOL) polyurethane. However, in an effort to meet current and anticipated Environmental Protection Agency (EPA) regulations as well as military requirements, the U.S. Army Research Laboratory (ARL) Weapons and Materials Research Directorate at Aberdeen Proving Ground, MD, has developed and patented a water reducible, two-component polyurethane coating for military vehicles that exhibits a 50% reduction in volatile organic compounds (VOCs) compared to the solvent-based system. Compared to the SOL formulation, the water-reducible (WR) polyurethane maintains required chemical agent resistance and exhibits superior properties.

This report will discuss coating properties such as flexibility, weather durability, hardness, impact, and mar resistance of both the WR and SOL systems. The coatings were also characterized using dynamic mechanical analysis (DMA), Fourier-transform infrared spectroscopy (FTIR), and desorption-gas chromatography/mass spectroscopy (D-GC-MS). Chemical characterization and mechanical evaluation lend insight into the relationship between molecular interaction during film formation and the resulting coating properties. The effect of coating dry time was investigated using DMA. FTIR was utilized to characterize "unaged" coatings and to better understand the effect of accelerated weathering on the chemistry of the WR and SOL coatings.

2. Background

The urethane polymer is formed by the reaction of a hydroxyl-terminated polyol with a diisocyanate, as shown in Figure 1. Solvent-based systems are formulated with a slight excess of
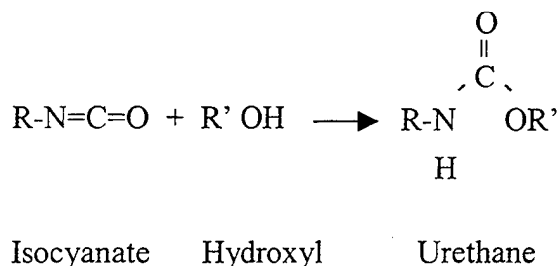
$$\text{R-N=C=O} \;+\; \text{R' OH} \;\longrightarrow\; \underset{\text{H}}{\overset{\overset{\displaystyle O}{\overset{\|}{C}}}{\text{R-N}}}\;\;\text{OR'}$$

Isocyanate   Hydroxyl   Urethane

Figure 1. Reaction of NCO With a Polyol to Form a Polyurethane.

isocyanate (NCO). NCO to OH ratios equal to approximately 1.1:1.0 are typical for solvent-based polyurethane coating formulations. The excess NCO ensures complete reaction of the polyol and provides optimal film properties. Great care is taken to ensure that excess moisture is not present in nonaqueous, two-component polyurethane formulations due to its undesirable reaction with NCO [1, 2]. NCO can also react with water, as shown in Figures 2 and 3. When this reaction occurs, an unstable carbamic acid is formed, resulting in CO_2 and amine. Carbon dioxide causes foaming and porosity in the film, and the amine can further react with NCO, forming urea. In short, the resulting film exhibits lower molecular weight and poor properties.

Recent developments in water-borne polyurethane technology have enabled high-performance coatings to be formulated using water-dispersible polyisocyanates and hydroxyl-functional polyurethane dispersions [3]. Hegedus et al. [4] recently proposed a mechanism for film formation of two-component, water-borne polyurethane systems. The mechanism suggests that the reaction between the NCO and water is sluggish compared to the reaction between NCO and the hydroxyl-terminated polyol, enabling urethane to form [4, 5]. In water-borne formulations, greater excess of NCO is required to account for the competing reaction between NCO and water. Typically, water-borne formulations are indexed using excess NCO ranging from 1.5 to 3.5. Early efforts within our laboratory focused on formulations with NCO to OH ratios of 2.0:1.0 and 3.5:1.0. While these films exhibited enhanced properties compared to the solvent-based coating, they did not have the necessary chemical resistance to pass the Army's requirement for nerve and blistering
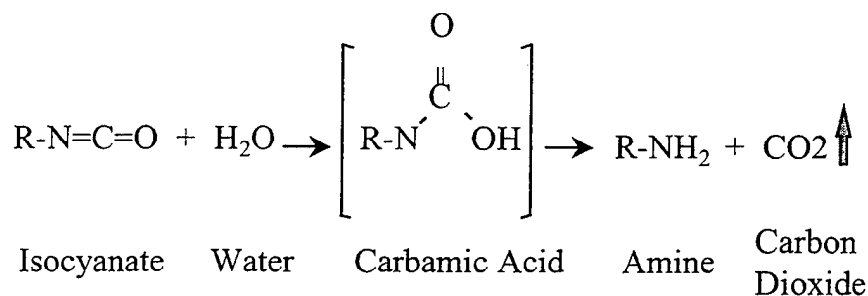
$$R\text{-}N\text{=}C\text{=}O + H_2O \longrightarrow \left[R\text{-}N \overset{\overset{\displaystyle O}{\overset{\|}{C}}}{} OH \right] \longrightarrow R\text{-}NH_2 + CO_2 \uparrow$$

Isocyanate   Water   Carbamic Acid   Amine   Carbon Dioxide

Figure 2. Reaction of NCO With Water to Form Carbamic Acid, Which Generates CO_2 and an Amine.

$$R\text{-}N\text{=}C\text{=}O + R'NH_2 \longrightarrow R\text{-}N \overset{\overset{\displaystyle O}{\overset{\|}{C}}}{\underset{H}{|}} \underset{H}{\overset{|}{N}}R'$$
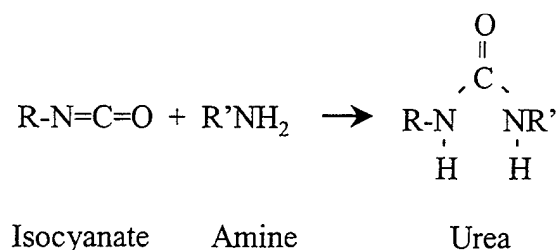
Isocyanate   Amine   Urea

Figure 3. Reaction of NCO With an Amine to Form a Urea.

agents. For this reason, further investigation led to the most recent formulations with NCO to OH ratios of 5.0:1.0. This level of indexing provided chemical agent resistance without a significant change in coating properties.

Even though urethane forms in the water-dispersible formulations, other reactions producing amine and ureas are also prevalent (Figures 2 and 3). Additionally, because of the excess NCO in these systems, crosslinking reactions that form allophanate and biuret are also likely. Crosslinking reactions of urethanes and ureas with NCO are shown schematically in Figures 4 and 5. It is a likely assumption that the cumulative effect of the side reactions occurring during the film formation of the water-dispersible coatings results in films with less uniform or more heterogeneous crosslinks than those from solvent-based films. Evidence suggesting heterogeneity of crosslinks in the WR coatings is provided by results from DMA and FTIR analyses.
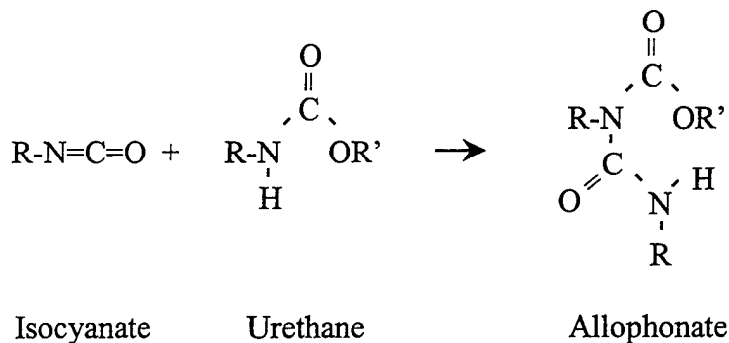
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$$\text{R-N=C=O} \;+\; \underset{\substack{| \\ H}}{\text{R-N}}\overset{\displaystyle \overset{O}{\underset{\|}{C}}}{}\text{OR'} \;\longrightarrow\; \text{Allophonate structure}$$

Figure 4 reaction: R-N=C=O + Urethane → Allophonate

| Isocyanate | Urethane | Allophonate |

Figure 4. Reaction of NCO With Urea to Form an Allophonate.

Figure 5 reaction: R-N=C=O + Urea → Biuret

| Isocyanate | Urea | Biuret |
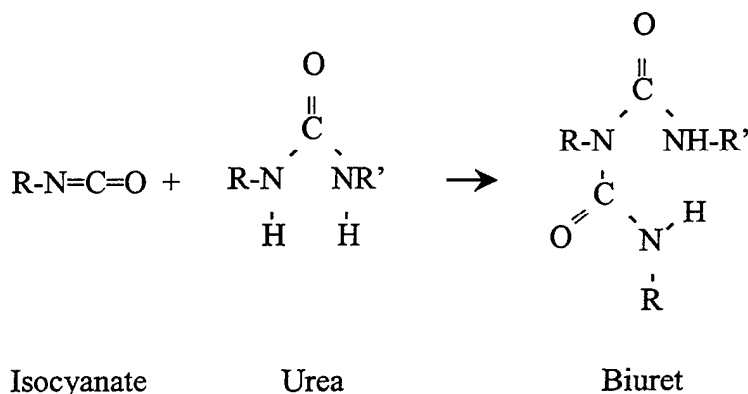
Figure 5. Reaction of NCO With Urea to Form a Biuret.

3. Experimental

The coatings were sprayed onto cold rolled steel panels pretreated with zinc phosphate (Bondrite 37) and a chromate sealer (Parcoolene 60), unless otherwise noted. The panels were sprayed to a dry film thickness of 45–55 μm. Formulations were pigmented according to color number 34094 (green 383), as stated in MIL-C-46168D [6], the U.S. Army specification for two-component polyurethane coatings. Water-reducible formulations were designated WR, followed by the specific NCO indexing. The solvent-based system was designated as SOL. Tests on coated panels were conducted according to MIL-C-46168D [6]. WR formulations implement water-dispersible hydroxy-functional polyurethane (PUR) and water-dispersible polyisocyanates with

conventional siliceous-type extenders for flattening purposes, as well as prime pigments used to make the base green camouflage coating. Tests on coated panels were conducted after varying dry times. The specific dry times were 7 days, 10 days, 17 days, 24 days, and 6 months. The coatings were exposed to accelerated weathering 2 months after they were sprayed.

Table 1 lists the general coating tests specified in MIL-C-46168D [6]. The procedures for each test are detailed in the military specification. Chemical agent resistance (CAR) was determined by subjecting the coated panel to the liquid agent, bisdichloroethyl sulfide (mustard gas), and allowing the sample to sit for 30 min. The surface of the panel was then rinsed with isopropanol. The residual agent vapor was then collected using bubblers at 4 hr and again after an additional 18 hr following the isopropanol rinse. The residual vapor after each interval was reported in ug.

Two types of accelerated weathering were conducted on the coated panels. EMMAQUA-night time weathering (NTW) exposure testing was performed in accordance with ASTM D4141-95 [7], Procedure C. The panels were subjected to 4 water spray cycles/hr. Each spray cycle lasted for 3 min. Spray cycles were conducted daily between 7 p.m. and 5 a.m. The specimens were mounted unbacked in an aluminum frame with the painted surface toward the reflective mirrors. Specimens were rotated at periodic intervals to ensure uniform exposure. Ultraviolet (UV) testing was conducted using a QUV weathering machine according to test method ASTM G53-96 [8]. A UVA 340 light source was used. Cycling involved 4 hr of light followed by 4 hr of condensation, for a total exposure time of 2,500 hr.

Color measurements were performed on a Huntlab Ultrascan spectrocolorimeter with a 6-in integrating sphere. The specular reflectance was included according to ASTM D2244-93 [9] and ASTM DE308-95 [10] with a 2° observer and illuminant C. FTIR analyses were performed using a Mattson Polaris spectrometer operating at a resolution of 4 cm^{-1} with external detector electronics. Microreflectance FTIR was used to obtain spectra of the chemical agent resistant coating (CARC) surface (i.e., about top 10 μ). Coupons sufficiently small to fit on a microscope slide were cut from the CARC panels and placed directly onto the infrared (IR) microscope stage. No other sample

Table 1. Selected Properties of Coated Panels

Sample	VOC $(\leq 420$ g/L$)^a$	CAR $(\leq 180$ µg$)^{a,\ b}$	Forward Impact Resistance (lb)	Low Temperature Flexibility$^{b,\ f}$	Color $(E_{NBS} \leq 2.0^g)^a$	Specular Gloss $(60° \leq 1.0)^a$ $(85° \leq 3.5)^a$
SOL	~420 g/L	~20 µg	$52,^c\ 48,^d$ 28^e	F	$E_{NBS} \sim 1.2$	$60° \sim 0.9$ $85° \sim 2.4$
WR 3.5	~180 g/L	~510 µg	$160,^c\ 148,^d$ 148^e	B	$E_{NBS} \sim 1.41$	$(60° \sim 0.9)^a$ $(85° \sim 1.7)^a$
WR 5.0	~180 g/L	~98 µg	$148,^c\ 84,^d$ 100^e	P	$E_{NBS} \sim 1.69$	$(60° \sim 0.9)^a$ $(85° \sim 2.2)^a$

[a] MIL-C-46168D [6] requirement shown in parenthesis.
[b] Data reported after 7-day dry time.
[c] Data reported after 10-day dry time.
[d] Data reported after 17-day dry time.
[e] Data reported after 24-day dry time.
[f] P = pass, B = borderline/pass, and F = fail. Failure is indicated by visible cracking in the coating after bending the coated panel around a cylindrical mandrel at 0 °C.
[g] Hunter's revised National Bureau of Standards (NBS) color difference equation.

preparation was needed (i.e., the method is nonintrusive). The reflectance spectra were obtained using a Spectra-Tech (Shelton, CT) microreflectance attachment with a 32 × IR objective and signal averaging of 256 scans. Background spectra were obtained using aluminum foil.

Thermal desorption-gas chromatography/mass spectrometry (D-GC-MS) was used to heat the coating samples in a pyroprobe at 175 °C for 20 s to release any unreacted NCO. The desorbed components were injected simultaneously through an interface onto a GC column for separation and passed through a mass spectrometer for identification. Desorption was achieved with a CDS Model 122 Pyroprobe (coil type) connected to a heated interface chamber to the splitless injector of a Hewlett Packard GC-FTIR-MS system (Model 5890 GC and Model 5970 mass selective detector). The pyroprobe interface temperature was 175 °C, and the sample was pulsed at 300 °C for 20 s. The GC column was a J & W Scientific capillary column (0.25 mm × 15 m; 0.25 µm DB5 film). The GC injector temperature was 200 °C. The oven temperature program used was 50 °C isothermal for 1 min and 70 °C/min to 250 °C for 11 min. The total run time was about 15 min; peaks generally eluted by 10 min. Reference NCO from a paint matrix elutes about 4 min after the air peak.

DMA was performed on nonsupported films using an Imass, Inc. autovibron (automated Rheo-200 rheovibron, Toyo Instruments). The samples were evaluated from – 100 °C to +150 °C at a heating rate of 2 °C/min. Data was collected at 1.1 Hz. DMA samples were prepared by spraying the coating onto release paper. The films were dried at ambient temperature (25 + 2 °C) for 10 days, 17 days, 24 days, and 6 months before separating them from the release paper. Coating film thickness varied between 160 μm and 280 μm. Data was normalized according to individual sample dimensions.

4. Results and Discussion

The properties of both the WR and SOL coatings have been previously reported [11]. Table 1 lists the properties of the two systems. MIL-C-46168D [6] requirements are indicated in parenthesis at the top of the table. WR 3.5 and WR 5.0 both pass all of the specification requirements, except that WR 3.5 does not meet the requirement for CAR. Both WR formulations exhibit vastly reduced VOC compared to the conventional solvent-based system. Additionally, the WR formulation exhibits superior forward impact resistance (FIR) and low temperature flexibility compared to the SOL coating. As coating dry time increases from 10 days to 24 days, the SOL coating lost nearly 50% FIR. WR 3.5 exhibited the best FIR retention with respect to coating dry time. Although FIR and low temperature flexibility are not MIL-C-46168D [6] requirements, they are important measures in coating wear durability.

Panels coated with WR 5.0 and SOL were exposed to a QUV 340A light source for 2,500 hr or accelerated outdoor weathering utilizing the EMMAQUA-NTW apparatus for a total radiant exposure of 280 MJ/m^2 and 560 MJ/m^2, respectively. The purpose of these tests was to verify the enhanced weathering resistance observed in previous accelerated exposure testing. Following accelerated aging exposure, the color change was measured, and FTIR and GC-MS analyses were performed. The color change observed in the coatings is shown in Table 2. WR 5.0 and SOL top coats were evaluated with both solvent-based and water-based epoxy primers. Compared to SOL in each of the respective exposures using both the QUV and the EMMAQUA test methods,

Table 2. Color Change Following Accelerating Aging

SAMPLE SYSTEM (Top Coat/Primer)	QUV 340A 2,500 hr (Δ Color ≤ 2.5)[a]	EMMAQUA 280 MJ/m^2	EMMAQUA 560 MJ/m^2
WR 5.0/solvent primer[b]	1.7	1.2	1.91
SOL/solvent primer[b]	7.4	3.80	7.61
WR 5.0/water primer[c]	2.5	2.18	3.83
SOL/water primer[c]	9.0	4.50	7.67

[a] MIL-C-46168D [6], specification requirement.
[b] MIL-P-53022B [12], solvent-based epoxy primer.
[c] MIL-P-53030A [13], water-based epoxy primer.

the data clearly indicates a more stable color retention (i.e., lower color difference) for WR 5.0. The data also suggests that the primer contributes significantly to the top coat durability. The solvent-based primer used with either top coat exhibited a lower color difference, suggesting a greater stability in color retention than when the water-based primer was used.

The spectra of WR 5.0 and SOL are shown in Figure 6. Major spectral bands are common to both systems, but there are differences. Pertinent infrared band assignments are provided in Table 3. WR 5.0 has distinct high frequency bands in the OH region at 3675 cm^{-2} and 3660 cm^{-2}, bands not found in the spectra of SOL. The solvent-based paint has a broader NH band (nom. 3400 cm^{-2}), which extends into the normal absorption region of the OH group. The presence of the sharp OH peak in WR 5.0 may be due to a sterically-hindered organic containing compound, such as OH, or to a hydrous silicate solids fill. The difference in baselines at frequencies below 2000 cm^{-2} made it necessary to apply baseline correction to the two spectra. In the spectrum of WR 5.0, there is a more distinct separation of the polyurethane and urea bands. There is a peak in the aromatic CH region in the spectrum of SOL that is much less evident in the WR 5.0 sample. The spectra indicated that unreacted NCO was not present near the surface of either coating, as evidenced by a lack of the prominent NCO band at 2270 cm^{-2}. The lack of NCO was confirmed with D-GC-MS at 300 °C. This method is very sensitive and confirmed that HDI was not present in significant quantities in either system.

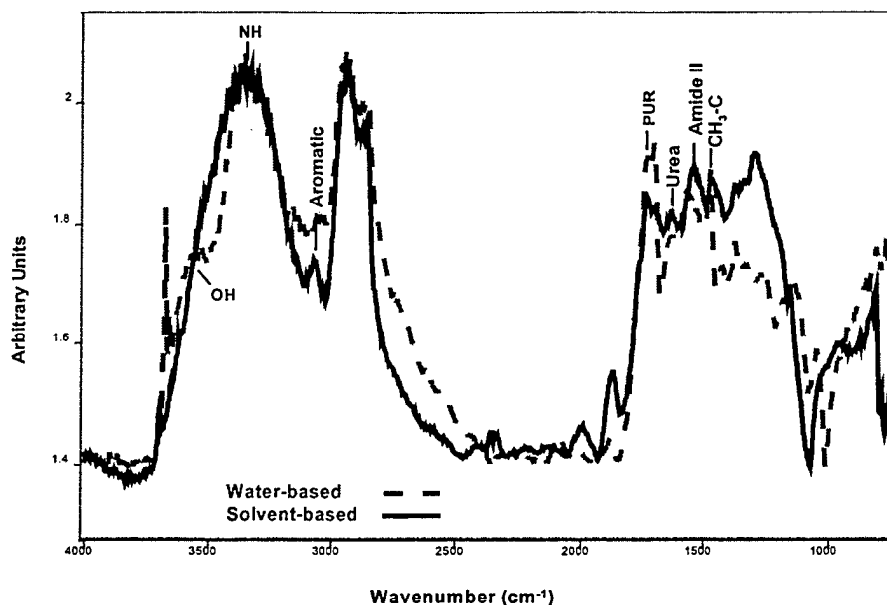**Figure 6. Spectra of Unexposed WR 5.0 and SOL Coatings.**

Table 3. Spectral Features of CARC

Wavenumber (cm^{-1})	Assignment
3650–3450	OH H-bond
3440–3200	NH &/or NH2 stretch
2980	CH3 asymmetric stretch
2930	CH2 asymmetric stretch
2860	CH2 asymmetric stretch
2280	NCO asymmetric
1765	Polyurethane, aromatic
1720–1740	Polyurethane, aliphatic
1685	Isocyanurate C=O
1650–1690	Urea C=O
1510–1560	Amide II
1465	CH2 scissoring
1460	Calcium-oxygen (strong band)
1375	CH3-C
1240–1280	Amide III
1250–1000	Silica (strong, very broad)
1220–1000	C-O-C stretch; strong but superimposed over silica band
1000–1250	C-C Skeletal vibrations; medium bands superimposed on silica band

Overlaid spectra of the UV-exposed samples and unexposed samples are shown for WR 5.0 and SOL in Figures 7 and 8, respectively. For comparison, the spectra were scaled so that the high-frequency (aliphatic) groups of the unexposed and UV-treated samples were of comparable magnitude. UV exposure appears to have a different effect on the WR 5.0 and SOL samples. The spectra of unexposed WR 5.0 exhibits comparable intensities of the aliphatic and polyurethane bands. After UV exposure, the PUR, amide, and urea bands appear to decrease in intensity relative to the aliphatic band. The N-H band broadens as a result of UV exposure. Unlike WR 5.0, the spectra for SOL (shown in Figure 8) suggests that the aliphatic band decreases in intensity relative to the PUR, amide, and urea bands.
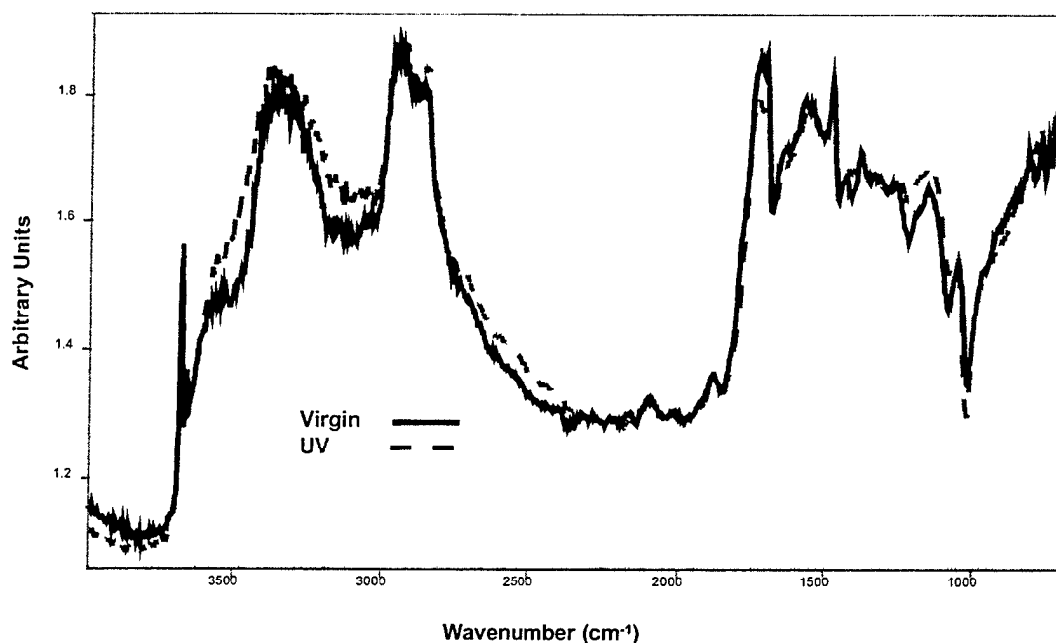
Figure 7. Spectra of Unexposed and UV-Exposed WR 5.0.

The spectra for the EMMAQUA-treated samples are shown overlaid with the unexposed samples for WR 5.0 and SOL in Figures 9 and 10, respectively. WR 5.0 exhibits broadening of the NH band after both UV and EMMAQUA testing; however, the effect is greater with the EMMAQUA-treated sample. This broadening may result from the hydrogen bonding association of water with the N-H

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Figure 8. Spectra of Unexposed and UV-Exposed SOL.

Figure 9. Spectra of Unexposed and EMMAQUA-Exposed WR 5.0.

Figure 10. Spectra of Unexposed and EMMAQUA-Exposed SOL.

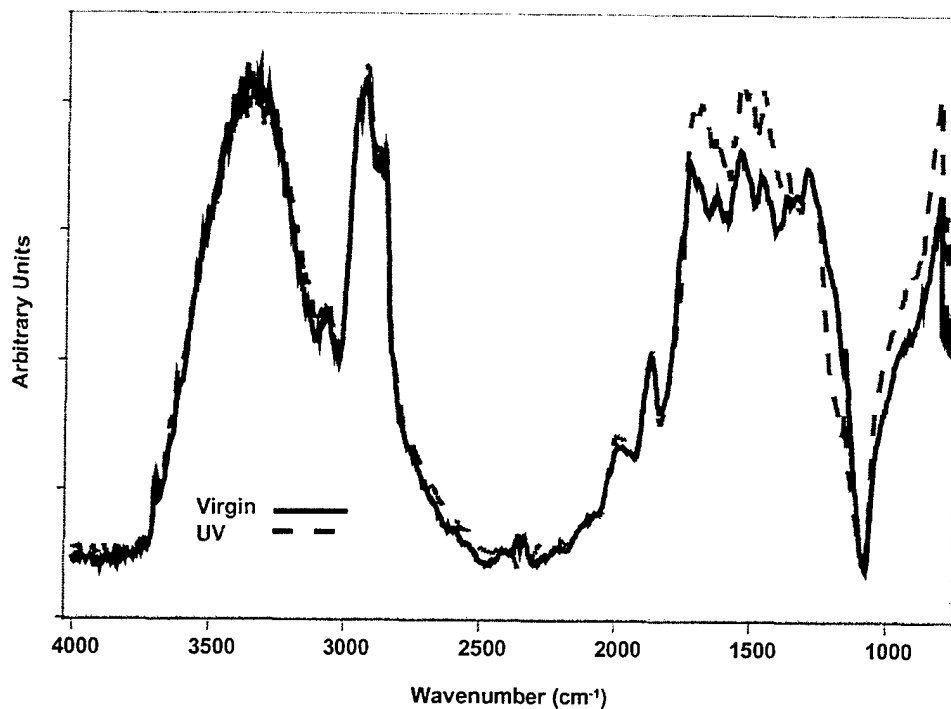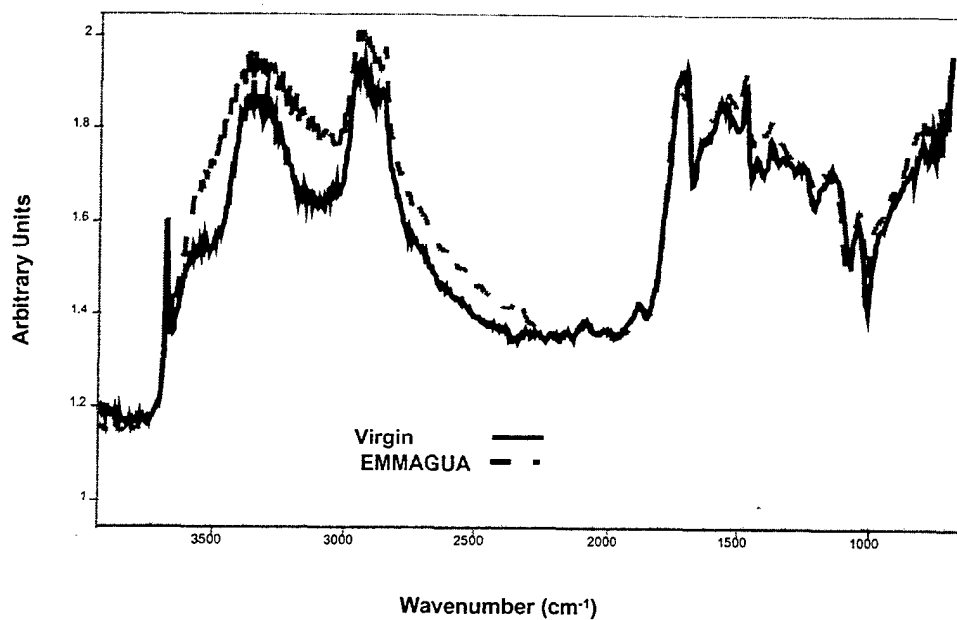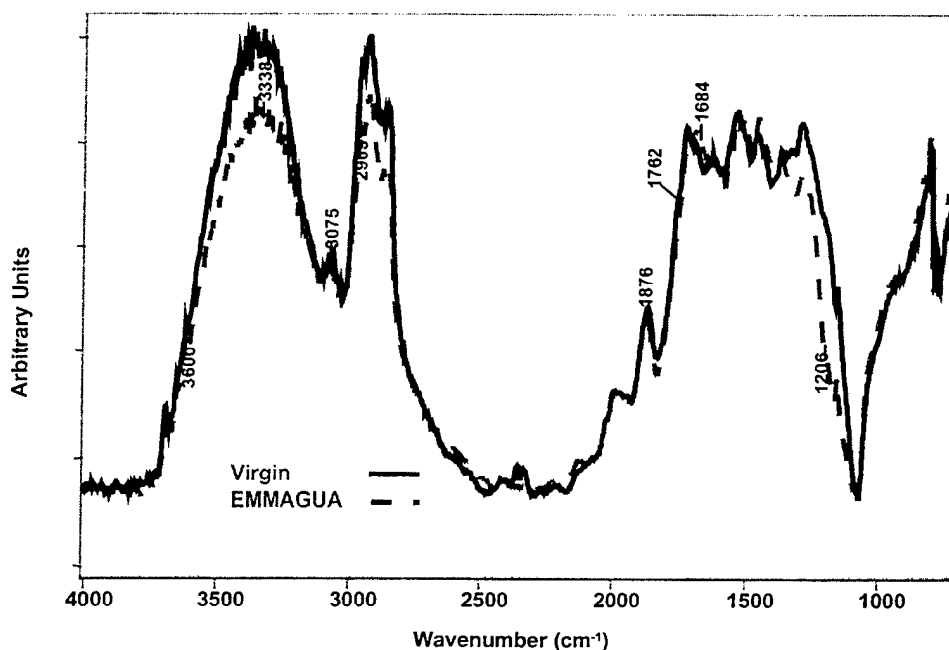region. The data therefore suggests that the effect of water on the coatings is greater following the EMMAQUA testing than it is following QUV testing. No change in the high-frequency shoulder of the carbonyl band was observed in the EMMAQUA sample, as had been observed with UV testing. SOL showed similar spectral changes in response to EMMAQUA and UV testing; the N-H, aliphatic, and aromatic peaks decreased in relative intensity to the PUR, amide, and urea bands. A decrease in the relative intensity of the aliphatic and N-H regions observed for SOL appears to correlate well with the significant color change observed following accelerated aging. Further work must be performed to confirm that such changes observed in the FTIR spectra relate to UV degradation. No broadening of the N-H region was observed following accelerated testing for the SOL coating. DMA data suggests that the SOL coating exhibits more uniform crosslinks compared to the WR samples. It is believed that this more homogeneous network results in greater CAR. Similarly, it may be more difficult for water to penetrate the SOL coating surface, thus explaining why broadening of the N-H region was not exhibited for SOL following accelerated aging.

Tan (δ) of the polyurethane coatings is shown in Figure 11. The solvent-based coating exhibits a much larger and sharper δ peak compared to the WR coatings. The temperature associated with the peak magnitude of δ is defined as the glass transition temperature (Tg). Following a 10-day dry time, the solvent-based system exhibits a significantly lower Tg (43 °C) than the WR coatings (73 °C). The sharper δ transition observed for the solvent-based coating suggests that it has more uniform crosslinks than the WR coatings. WR 3.5 exhibits the broadest δ transition of the three coatings, suggesting the greatest degree of heterogeneity of crosslinks. These results were also observed in the loss modulus (E') vs. temperature curves, as shown in Figure 12. WR 3.5 exhibits a very broad E' transition that is notably high over a broad temperature range (-98 °C to + 80 °C).
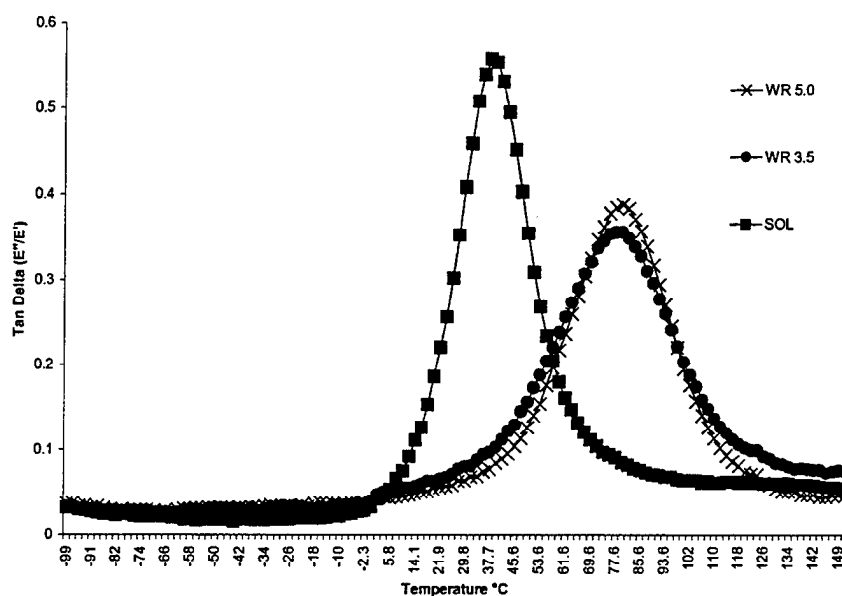
Figure 11. Tan Delta at 1.1 Hz After 10-Day Dry Time.

The E' transition of WR 5.0 is also broad compared to that of SOL. High values of E' suggest greater mobility of the polymer chains associated with dissipation of energy when the polymer is subjected to deformation [14]. Thus, coatings exhibiting a high and broad E' transition have the ability to absorb energy associated with impact. Therefore, the DMA data helps to explain the
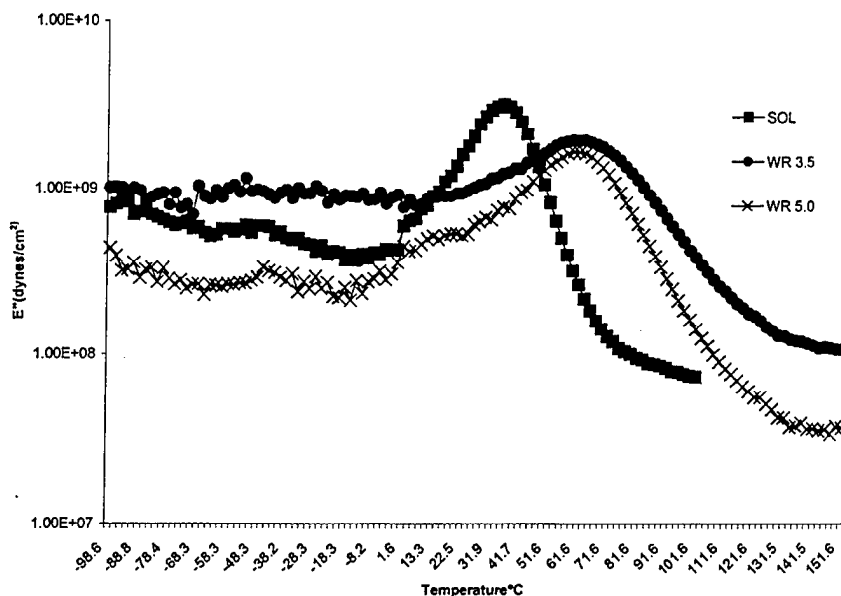
Figure 12. E' at 1.1 Hz After 10-Day Dry Time.

superior impact resistance of WR 3.5 and WR 5.0 compared to the solvent-based system. Although impact resistance was measured at ambient temperature (25 ± 2 °C), the DMA data suggests that in particular, WR 3.5 may also exhibit superior low-temperature impact resistance. The DMA data suggests that while broad loss transitions indicate superior mechanical properties such as impact resistance, sharper loss transitions (such as those exhibited by SOL) appear to be related to superior chemical agent resistance. Broad E' and δ transitions suggest nonuniformity of crosslinks in the water-reducible system [14–17]. Broad loss transitions have been previously observed in water-reducible systems [14, 18, 19]. Thus, Hegedus' [4, 5] research indicating the potential for side reactions and polyurethane formation are further explained by the broad loss transitions observed in this study. Such nonuniformity during film formation may introduce voids in the polymer matrix. The voids would allow a greater amount of chemical agent to penetrate and become trapped in the water-reducible coating than it would in the solvent-based systems. Therefore, DMA provides some insight into the fact that differences in crosslinking from film formation in the solvent-based and water-reducible coatings result in the optimization of different properties. The authors are unaware of other findings that qualitatively relate chemical agent resistance of paint to DMA loss properties.

While WR 5.0 currently provides the best balance of chemical and mechanical properties, WR 3.5 exhibits the most enhanced mechanical properties. Additionally, WR 3.5 requires less NCO to form the coating, which is an important cost consideration for full-scale production. It is interesting to note that while SOL exhibits a significantly lower Tg than the WR coatings, SOL exhibits poorer low temperature (0 °C) flexibility. At 25 °C, all three polyurethane coatings exhibit acceptable flexibility, as measured by bending the coated panel over a cylindrical mandrel (specified in ASTM D522 [20] Method B). The enhanced low temperature flexibility of WR 3.5 and WR 5.0 is believed to be the result of the broad loss transitions shown in Figures 11 and 12.

DMA was also used to study the effect of coating dry time on mechanical properties. The dynamic mechanical properties of SOL were found to be much more sensitive to coating dry time than were the WR coatings. After all dry times, E' in the rubbery plateau increased with increasing temperature for SOL, while the WR coatings exhibited a flat rubbery plateau throughout the experiment. This was most pronounced after 17- and 24-day dry times and less pronounced after the 6-month dry time for SOL. The observation of increased E' vs. temperature is shown in Figure 13 after a 24-day dry time. This data indicated that SOL was not fully crosslinked at dry times ≤ 24 days at ambient temperature. This data provides some explanation for the reduced FIR of SOL after a 24-day dry time. It appears that increasing dry time results in additional crosslinking, causing embrittlement of the SOL coating that is not observed in the WR coatings.

DMA evaluation was also conducted on both WR and SOL coatings after a 6-month dry time. In these experiments, SOL exhibited an increase in E' and a decrease in δ peak magnitude. This strongly suggests a notable increase in crosslink density after a 6-month dry time. Although WR 5.0 also exhibited increased E' after drying for 6 months, a negligible change in δ peak magnitude was observed. However, WR 5.0 exhibited a significant increase in Tg after the 6-month dry time. WR 3.5 was not evaluated after 6 months. DMA data for SOL and WR 5.0 coatings is shown in Table 4. The data suggests that while SOL may undergo increased crosslink density with respect to dry time, the changes in WR 5.0 are notably different. It is speculated that observed changes in DMA data for WR 5.0 after 6 months may indicate a densification in the coating. Densification
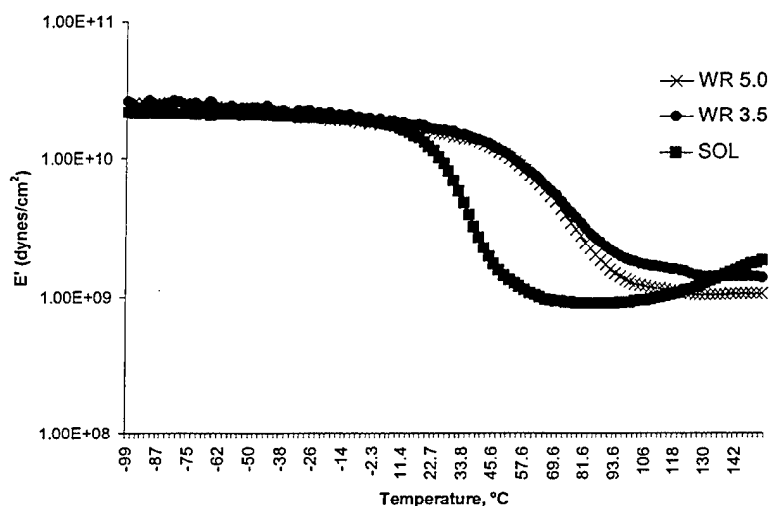
Figure 13. E' at 1.1 Hz of SOL After 24-Day Dry Time.

Table 4. DMA Data Measured at 1.1 Hz of SOL and WR 5.0 With Respect to Coating Dry Time

Sample	T_g (°C)	δ Peak Magnitude	E' (dynes/cm^2) at 100 °C
SOL 10d	43	0.584	1.06×10^9
SOL 6 Mo.	37	0.336	2.00×10^9
WR 5.0 10d	73	0.379	1.13×10^9
WR 5.0 6 Mo.	91	0.384	1.96×10^9

in coatings from physical aging has been observed by other researchers [16, 21]. The DMA data shows increased crosslink density of SOL after longer dry times, which may actually result in reduced mechanical performance due to brittleness associated with crosslinking. Evidence of this was mentioned earlier with respect to impact resistance. Evidence of densification observed for WR 5.0 may lead to enhanced chemical agent resistance without further compromising mechanical properties. Tests on coated panels after longer dry times are necessary to confirm the DMA results. Although the chemical agent resistance associated with SOL is desirable, chemical agent resistance is obviously irrelevant if the mechanical properties of the material cannot meet minimum durability requirements.

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5. Conclusions

The ARL Weapons and Materials Research Directorate has successfully developed a water-reducible CARC that meets MIL-C-46168D [6] specifications and exhibits a significant reduction of VOC compared to the currently used solvent-based polyurethane coating. The water-reducible coating formulation exhibits superior mechanical properties over the solvent-based system. While WR 5.0 meets chemical agent resistance requirements, WR 3.5 exhibits optimal mechanical properties that are important for long-term durability under broadly varying environmental conditions observed in service.

WR 5.0 and SOL samples crosslink by different mechanisms. The infrared spectra of these samples show distinct differences in the O-H, N-H, and PUR regions. The water-based spectrum has a distinct spike at 3,600 cm^{-1}, a spike not present in the solvent-based sample. The water-based sample has a greater separation of the PUR and urea bands, and a more narrow N-H band than is evident with the solvent-based sample. Neither coating showed evidence of unreacted NCO monomer at the surface, as determined by FTIR and D-GC-MS. Exposure to UV radiation apparently has a different effect on the two formulations. Evidence of decreasing intensity in the aliphatic and N-H regions for SOL allude to a possible mechanism of UV degradation. WR 5.0 exhibits broadening in the N-H region, which is suggestive of water interaction with the polymer matrix. More work is being done to determine which mechanisims are operative as a result of accelerated weathering.

DMA provided insight into the different chemistries associated with film formation of the solvent-based and water dispersible formulations and the affect of dry time on the dynamic mechanical properties of the coatings. The type of crosslinking required for superior chemical agent resistance is different than that required to optimize mechanical properties. Compared to WR 3.5, WR 5.0 may exhibit improved chemical agent resistance and therefore sharper loss transitions because of the additional crosslinking associated with the excess NCO present in the WR 5.0 formulation. The more highly crosslinked film may exhibit fewer voids that can trap chemical

agents. The dynamic mechanical properties of SOL were shown to be much more sensitive to dry time than the WR coatings, which may adversely affect coated panel properties of the solvent system in service. Future work is planned to evaluate both WR and SOL coated onto test panels. Determining the mechanical properties, such as impact resistance, low temperature flexibility, and chemical agent resistance (with respect to aging and the use of different primers) with the WR and SOL formulations is also planned.

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Polyurethane coatings used as camouflage and protective "top coats" for Army tactical vehicles and aircraft have been characterized and evaluated for performance criteria. A two-component water-reducible and a one-component solvent-based polyurethane coating have been investigated. The water-reducible (WR) coating was developed and patented by the U.S. Army Research Laboratory, Weapons and Materials Research Directorate at Aberdeen Proving Ground, MD; it exhibits a 50% reduction in volatile organic compounds (VOCs) compared to the solvent-based (SOL) system. Compared to the solvent-based formulation, the WR polyurethane maintains required chemical agent resistance and exhibits superior properties. The coating performance properties investigated include flexibility, weather durability, hardness, impact, and mar resistance. The coatings were characterized using dynamic mechanical analysis (DMA), Fourier-transform infrared spectroscopy (FTIR), and desorption-gas chromatography-mass spectroscopy (D-GC-MS). Chemical characterization and mechanical evaluation lend insight into the relationship between molecular interaction during film formation and the resulting coating properties. The effect of coating dry time was investigated using DMA. FTIR was utilized to characterize "unaged" coatings and to better understand the effect of accelerated weathering on the chemistry of the WR and SOL coatings.

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